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STUDY OF MICROMECHANICAL PROPERTIES OF ADHESIVE BONDED JOINTS

Contract No. DAAA 21-67-C-G500

THIRD QUARTERLY PROGRESS REPORT
(1 January 1968 - 31 March 1968)

By:

Edward J. Hughes and John L. Rutherford
Metallurgy and Ceramics Section
Materials Department

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Submitted to:

PLASTICS AND PACKAGING LABORATORY
FELTMAN RESEARCH LABORATORY
PICATINNY ARSENAL
DOVER, NEW JERSEY

15 APRIL 1968

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Approved by:

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ABSTRACT

This is the third quarterly report of a program to measure the mechanical properties of adhesive bonded joints, utilizing General Precision's advanced high precision microstrain techniques. During the current report period, progress was noted as follows:

1. The effective tensile modulus (E^*) of Epon 9601 was measured over a temperature range of -100° to 235°F using stainless steel and aluminum adherends. The highest values of E^* were found with stainless steel adherends and no carrier in the 9601. When the nylon carrier was used, E^* values were lower over the whole temperature range, with the lowest numbers obtained with aluminum adherends.
2. E^* for Epon 9601, with carrier, on aluminum adherends was found to decrease with increasing pre-strain. It dropped from 725,000 to 614,000 psi at a pre-strain of 20×10^{-4} .
3. The tensile secant modulus of Epon 9601, with carrier, on stainless steel adherends was found to increase as the cross head speed was increased at temperatures above 150°F . At lower temperatures there was no observable effect as the cross head speed was changed.
4. The precision elastic limit (P.E.L.) for tensile tests of Epon 9601, with carrier, on aluminum adherends was found to be temperature dependent. The P.E.L. was highest at the lowest temperature (-10°F) and showed a marked decrease as the specimen was warmed to 55°F . From that temperature to about 125°F the P.E.L. was relatively independent of temperature. Above 140°F , there was no discernible precision elastic limit.

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FOREWORD

This report has been prepared by the Materials Department, General Precision Aerospace Research Center, Little Falls, New Jersey under Contract No. DAAA 21-67-C-0500. Dr. John L. Rutherford, Senior Staff Scientist was the Program Manager. The Principal Investigator was Dr. Edward J. Hughes, Staff Scientist; he was assisted by Mr. Fred C. Bossler, Research Assistant. Mr. Kenneth J. Zwoboda, Supervisor, Research Model Shop and Design was responsible for all machining. Mr. Charles W. Bing, Senior Design Engineer, made significant contributions to the design of the testing apparatus. The work is being administered under the direction of the Plastics and Packaging Laboratory, Feltman Research Laboratory, Picatinny Arsenal, Dover, New Jersey, with Mr. Michael Bodnar acting as Contract Project Officer.

This Third Quarterly Progress Report covers the period 1 January 1968 to 31 March 1968. The results presented in this report represent work in progress and may be subject to revision as the program continues.

1. INTRODUCTION

This report is a summary of work performed during the period, 1 January 1968 to 31 March 1968, in which an advanced high precision microstrain approach to the characterization of adhesive properties was applied to selected adhesive systems. In a prior six-month pilot study, General Precision Systems Inc. demonstrated the feasibility of these microstrain techniques for the measurement of deformation of thin adhesive-bonded joints. The present contract effort is the utilization of these techniques to determine the effect of joint thickness, curing agents, filler content and temperature on the tensile, compression and shear moduli, fracture strength, precision elastic limit and mode of failure in selected adhesive systems. From measurements of adhesive deformation resulting from tensile, compression and shear loading it is possible to determine the state of strain in both the adhesive material and in the adherends. This information is necessary to obtain optimum performance of adhesive bonded joints.

The microstrain technique of General Precision Systems Inc. employs a capacitance type extensometer which operates in two different configurations. In one case, an air gap capacitor is mounted on the tension/compression adherends, straddling the adhesive joint. As the specimen is loaded the capacitance changes because the distance between capacitor plates is altered. The resolution of this device is on the order of 10^{-7} inch. The second case uses the tensile/compression adherends as the capacitor plates with the adhesive material as the dielectric medium between them. This configuration, which has an extension sensitivity on the order of 5×10^{-8} inch, does not record the deformation in the adherends. The observed extension is that due to the adhesive alone. The simultaneous use of both techniques provides a powerful tool for the study of the effect of strain on the electrical properties of adhesive materials.

Shear data are obtained by attaching the air gap extensometer to napkin ring type adherends. Angle of twist sensitivities on the order of 6.1×10^{-8} radians are routinely obtained.

2. EXPERIMENTAL PROCEDURE

A new, larger environmental test chamber has been installed on the crosshead of the Instron Tensile Testing Machine. The chamber is large enough to house the torsion testing assembly, including the yoke that is used to attach the two loading chains to the load cell. The operating temperature range is -100°F to 375°F . High temperature testing is done in air, while the low temperature work uses an atmosphere of carbon dioxide gas. Temperature is controlled to $\pm 1/2^{\circ}\text{F}$; the ambient temperature is measured as well as the specimen temperature. Since calibration of the extensometers at other than room temperature is difficult, indirect methods had to be employed. The basic technique is to feed the output of the load measuring extensometer into the X axis of the recorder, and to put the signal from the Instron load cell into the Y axis. After the specimen load reaches several hundred pounds, the recording is a straight line. This straight line is the relationship between applied load and the output of the load measuring extensometer which is mounted on the napkin-ring adherend adjacent to the epoxy joint. The same type of recording is made at the various test temperatures. The differences in the recordings as the temperature is changed are due to two principal effects: 1. the shear modulus of the metal adherend decreases as the temperature is increased; this should increase the extensometer output because the adherend deformation will be greater for a given load; 2. due to thermal expansion of the various parts, the gap between the capacitor plates may change which alters the extension sensitivity and the resultant output. Over a temperature range of 250°F , the load calibration changes about 20%. As the temperature is lowered, the shear modulus of the steel increases, thus the extension is smaller (for a given load) and the voltage output is less. This effect contributes only a small amount to the temperature dependence. The major change results from an increased capacitor plate separation as the temperature is lowered. A larger plate separation means lower sensitivity or a smaller output for a given applied stress. The mounting geometry is the same for the load measuring extensometer (across the adherend alone) as for the extensometer used to measure the angle of twist (across the epoxy joint). Thus the plate separation due to changing temperature is the same in each case. In other words, this calibration change is the

same for both extensometers. The two outputs go to the X and Y axes of the recorder and are such that the two changes in sensitivity cancel each other. That is, a stress-strain curve drawn at one temperature would have the same slope as another made at a higher temperature if the epoxy modulus was not temperature dependent (neglecting the 4% error introduced by the temperature dependence of the metal adherend).

All of the data presented in this report for Shell Epon 9601 used a cure cycle of 224°F for 2 1/4 hours. Different pressures were used to obtain a variety of joint thicknesses. Aluminum and stainless steel adherends were used; in each case the metal is identified. While data are presented for individual specimens in this report, duplicate (and more) specimens were often tested. The final report will include the range of values for these measurements.

As used in this report, the secant modulus is defined as the slope of a straight line drawn on a stress-strain curve that connects the origin of the curve with a particular stress value. If the stress-strain curve was linear, indicating elastic deformation, then the secant modulus would have the same value as the elastic modulus. Whenever viscoelastic or plastic behavior is part of a stress-strain curve then the secant modulus (drawn to a stress higher than the yield point) is always less than the elastic modulus.

3. RESULTS AND DISCUSSION

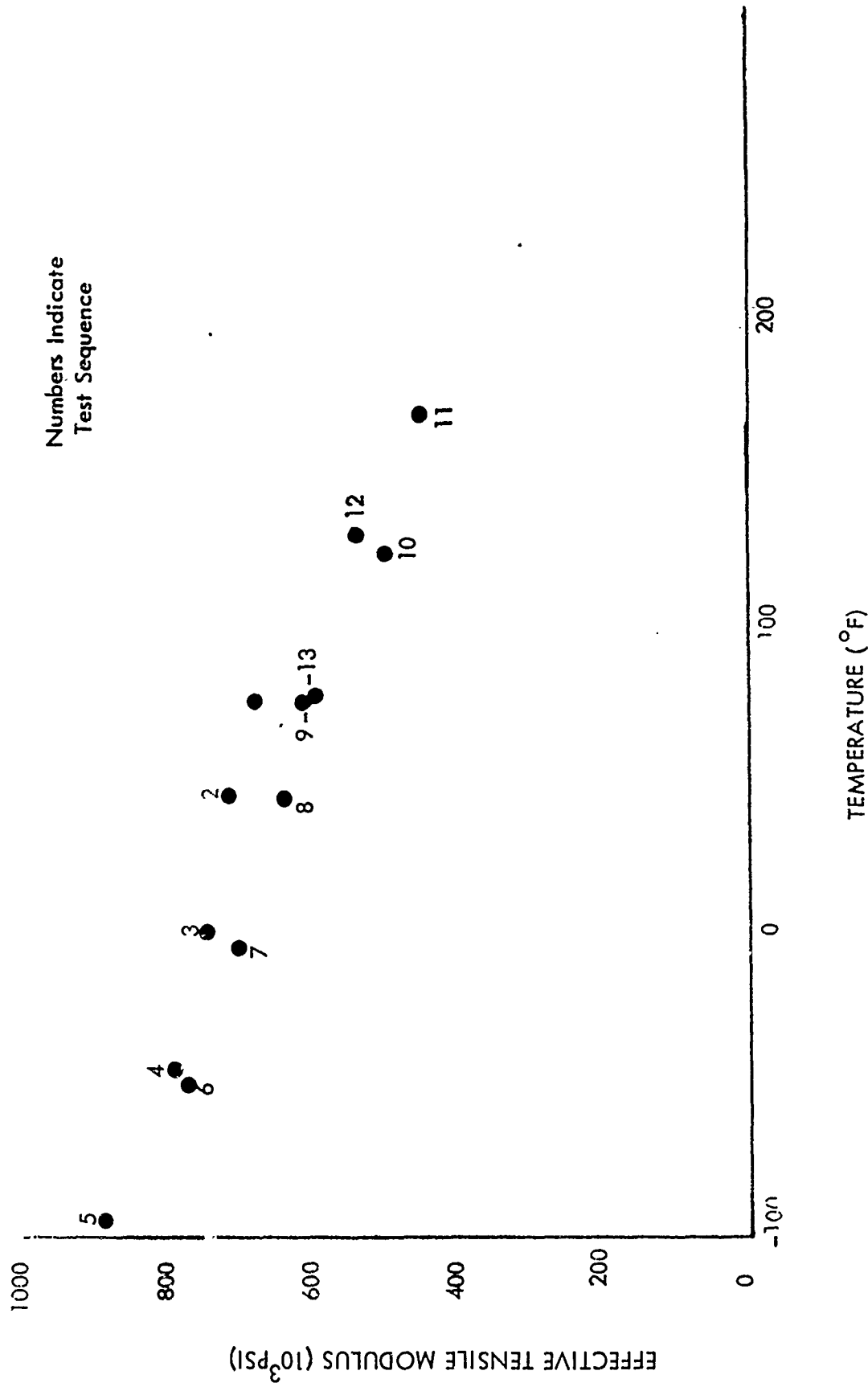
3.1 Temperature Dependence of Effective Tensile Modulus

The effective tensile modulus (E^*) of Epon 9601 was determined as a function of temperature or both stainless steel and aluminum alloy adherends. Epon 9601 was obtained in the form of a tacky tape consisting of nylon cloth impregnated with adhesive and covered with separator sheets to prevent adhesion to itself. Samples of the tape, both with and without nylon carrier, were generously supplied by the Shell Chemical Co., Adhesives Dept., Pittsburg, Calif. Three specimens were tested as a function of temperature. Details are given below:

- 1) aluminum adherends - Epon 9601 with nylon carrier
- 2) stainless steel adherends - Epon 9601 with nylon carrier
- 3) stainless steel adherends - Epon 9601, no carrier

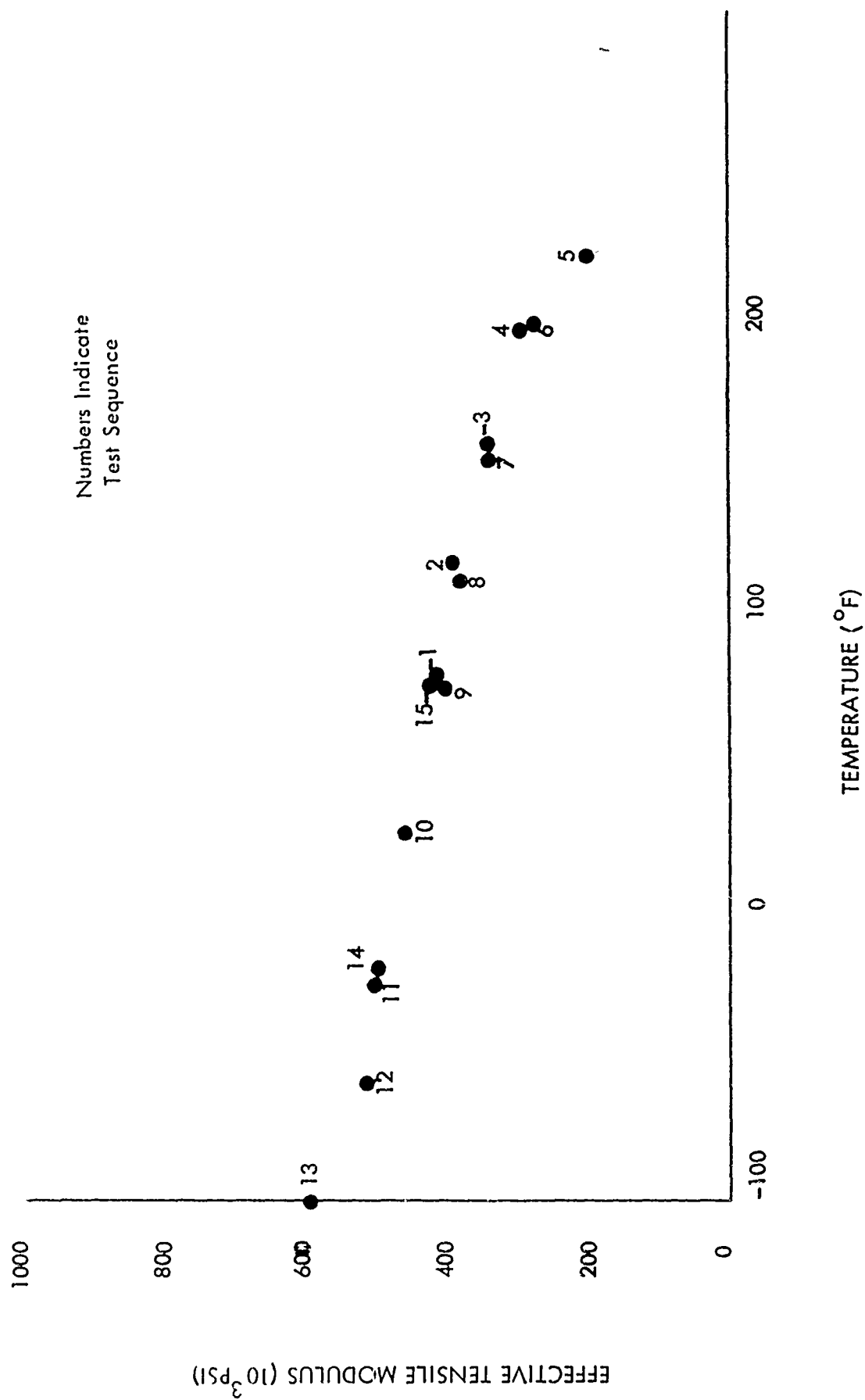
The two specimens in which a carrier was used were both prepared using a 0.001 inch thick tape. Both were cured for 2 1/4 hours at 224°F in the manner previously described in the First Quarterly Progress Report. The specimen without the carrier was prepared using two thicknesses of 0.005 inch thick tape and cured under identical conditions to those outlined above.

All of the specimens were tested in an environmental chamber mounted in the Instron tensile machine. In a typical test, load extension curves were drawn at room temperature up to approximately 80% of the fracture stress. The joint was then cooled in a step-wise fashion to -100°F, with load-extension curves being drawn at several temperatures. The specimen was then reheated in a similar manner through room temperature up to 235°F. Finally it was cooled down to room temperature. At each temperature, the specimen was allowed to reach equilibrium before carrying out the load unload tests. The variation of the effective tensile modulus over the temperature range investigated is shown for each of the specimens in Figures 1, 2 and 3. In each of these diagrams, the numbers beside the experimental points refer to the sequence of the load-unload measurements. The modulus values shown were calculated between stresses of 500 and 1500 psi where the adhesives were still deforming elastically. Above about 150°F, there was no elastic deformation



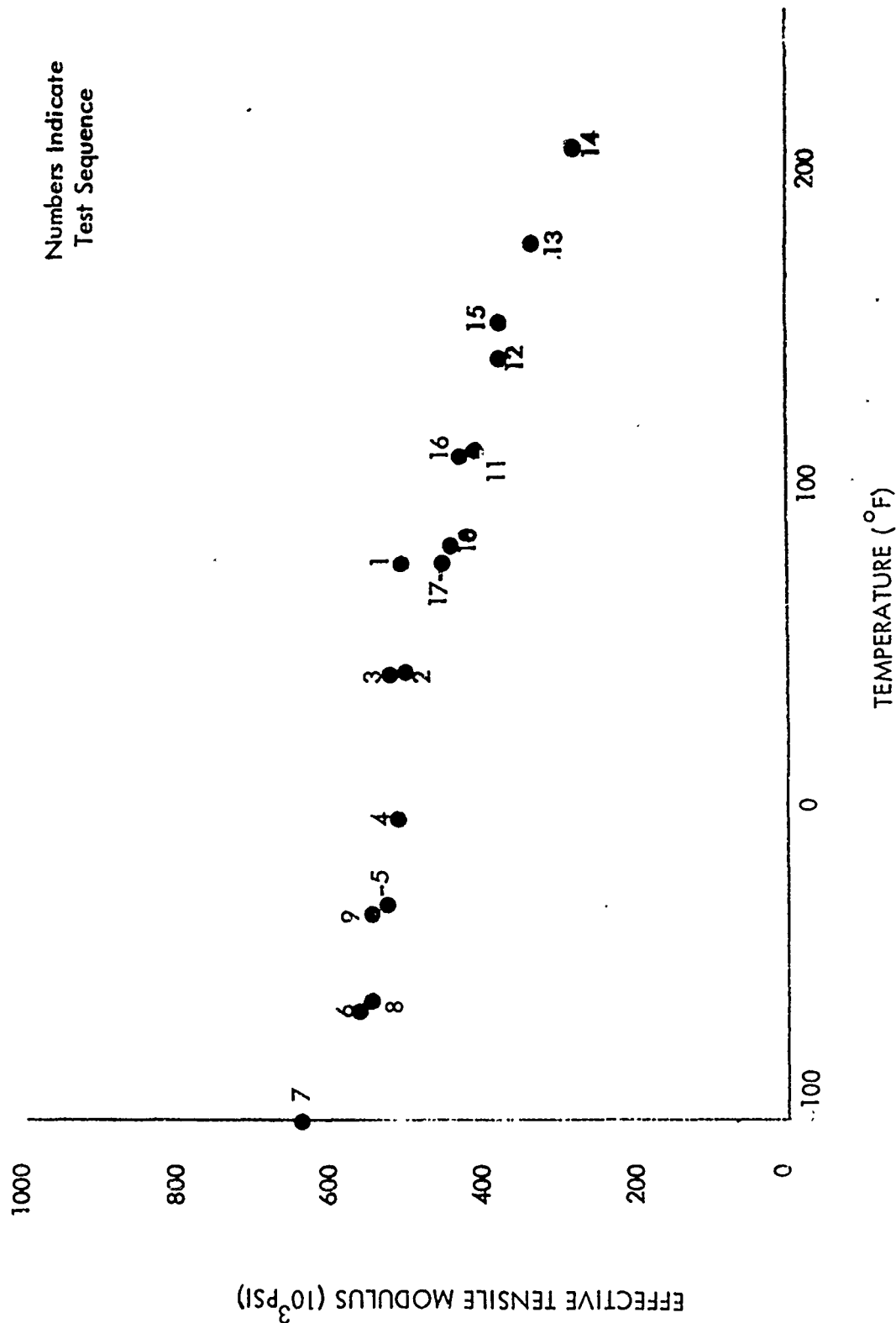
TENSILE TESTS-EPON 9601, WITHOUT CARRIER, STAINLESS STEEL ADHERENDS

FIGURE 1



TENSILE TESTS-EPON 9601, WITH CARRIER, ALUMINUM ADHERENDS

FIGURE 2

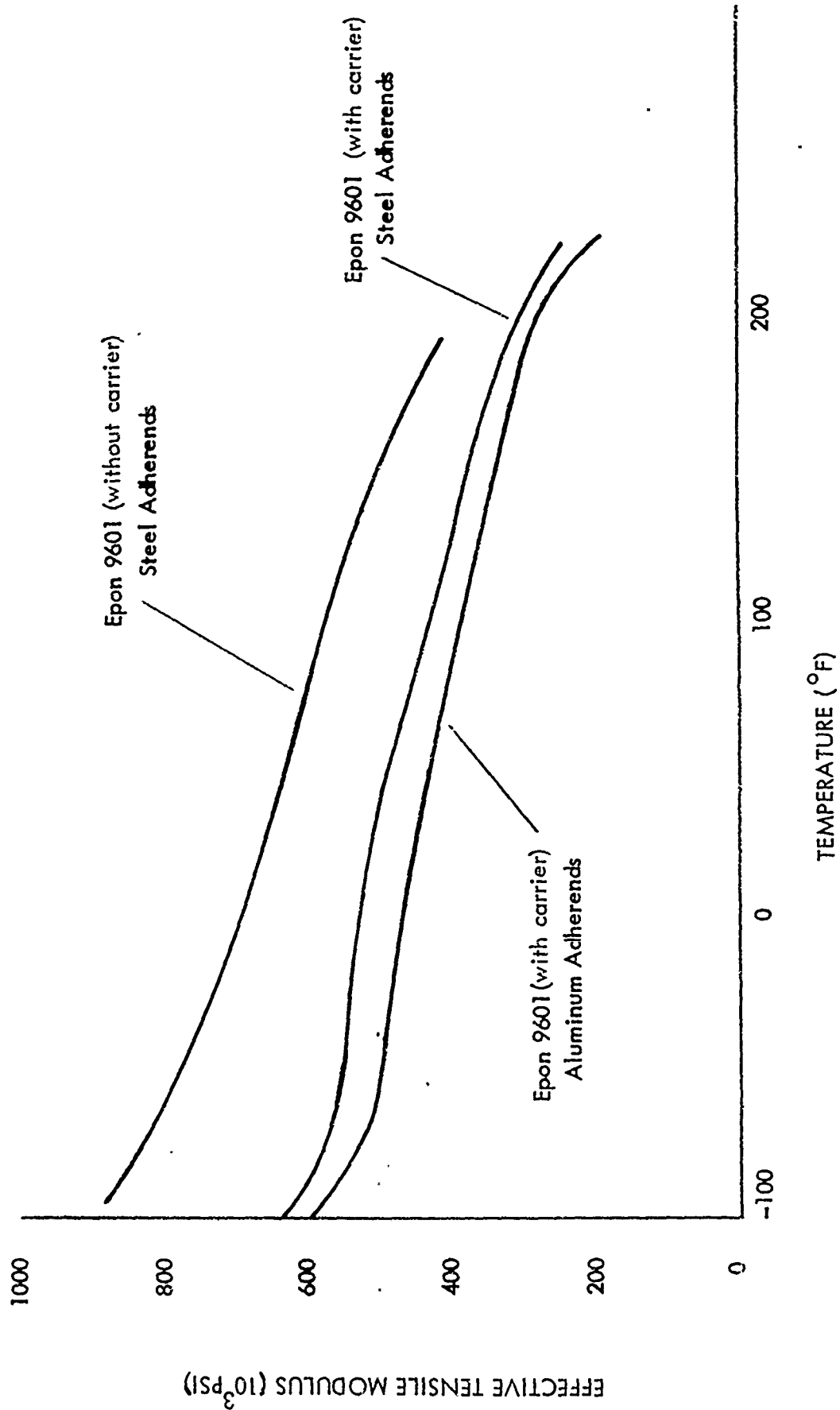


TENSILE TESTS-EPON 9601, WITH CARRIER, STAINLESS STEEL ADHERENDS

FIGURE 3

even at low stresses; the values reported there are for secant moduli. The general behavior for each of the three specimens was the same; that is, the tensile modulus decreased progressively with increasing temperature up to approximately 200°F. Above this temperature, the modulus decreased rapidly due to a large amount of plastic flow and viscoelasticity at these high temperatures. In addition, below approximately -75°F a large increase in E^* was observed. In all cases, the appropriate corrections were made for the extension of the adherends. The two specimens in which a nylon carrier was used (Figures 2 and 3) showed little or no hysteresis on the heating/cooling cycle. The third specimen (no carrier) did show a small amount of hysteresis (Figure 1). The temperature/effective tensile modulus relationship for all three specimens is given in Figure 4, where it can be seen that both the adherend material and the carrier influence the absolute values of E^* . The thin film joint using stainless steel adherends has a consistently higher modulus than when aluminum adherends are used. Kwei et.al.* have shown that the mechanical properties of thin polyolefin films are influenced by both the curing conditions and the nature of the substrate. They proposed that the modulus changes in thin films were due to surface layers which originated during the cooling of the polymer melt during solidification and an interior region whose properties approached those of the bulk material. The increase in modulus on going from stainless steel to aluminum alloy adherends observed in the present work can be ascribed to a modification of the structure of the epoxy adjacent to the adherends which occurs during the curing and solidification of the epoxy. The surfaces of aluminum and steel are vastly different, since the former has an oxide layer on the surface, which would be expected to influence the epoxy in a manner different from that of the steel. An alternate explanation was given in the Second Quarterly Progress Report: due to mechanical constraints, the higher the modulus of the adherends, the higher the effective tensile modulus of the adhesive material. The rapid decrease in the effective tensile modulus at temperatures above 200°F is observed in polymers at

* Kwei, T.K., Schonhorn, H., and Frisch, H.L., (1967), J. Appl. Phys., 38, 2512



temperatures which depend on the particular system. In the present case, it is probably due to approaching the glass transition temperature. The transition allows uncoiling of polymer chains on mechanical loading; resulting in a material with a lower E^* .

The higher modulus values associated with the epoxy joints not containing the nylon cloth carrier may be due to several reasons. The specimen with no carrier had a joint thickness of 10.25×10^{-3} in. compared with 13.25×10^{-3} in. for the bond with the carrier.

Previous work in this program has shown that the E^* for thin films of Epon 828-Versamid 140 (30 wt %) between stainless steel adherends decreased with increasing thickness. For that system, a change in thickness from 10.25×10^{-3} in. to 13.25×10^{-3} in. resulted in a decrease in E^* at room temperature of only 2-3% compared with approximately 15% for the Epon 9601. Although the magnitude of this effect will vary from system to system, it seems unlikely that it can account for a 15% decrease in modulus, although it is probably a contributing factor. The major cause of the decreased E^* probably lies in the presence of the nylon carrier. Earlier work in this program has shown that reinforcing agents, additives, or fillers often decrease the effective tensile modulus; probably by introducing mechanisms that provide for time-dependent deformation characteristics.

3.2 Pre-strain Dependence of Effective Tensile Modulus

It has been observed in many specimens that the effective tensile modulus (E^*) decreases following each increment of permanent strain. This relationship is shown, quantitatively, in Figure 5. The data were obtained from tensile tests made with aluminum adherends bonded together with Epon 9601 (with nylon cloth carrier). The sheet adhesive was nominally 0.010 inches thick prior to bonding; after curing at 224°F for 1 1/4 hours under slight pressure (about 10 psi) the glue-line was 8.75×10^{-3} inches thick. All tests shown in Figure 5 were made at room temperature at an Instron cross head speed of .05 inches per minute. The term "pre-strain" is used to describe the resultant strain a few minutes after completing a load-unload cycle. Usually there is a small amount of strain recovered when the specimen is unloaded and allowed to remain with only the bias

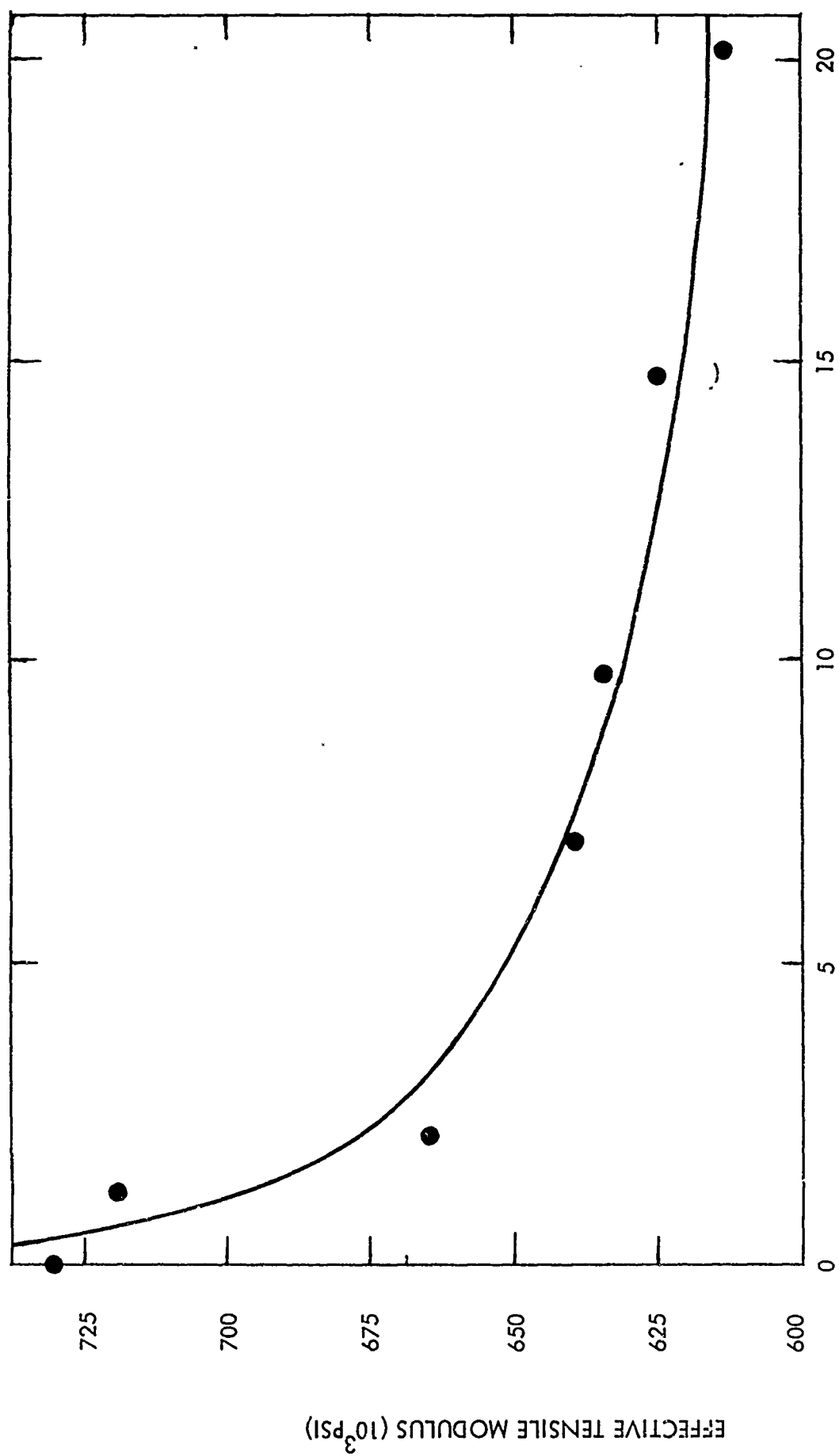


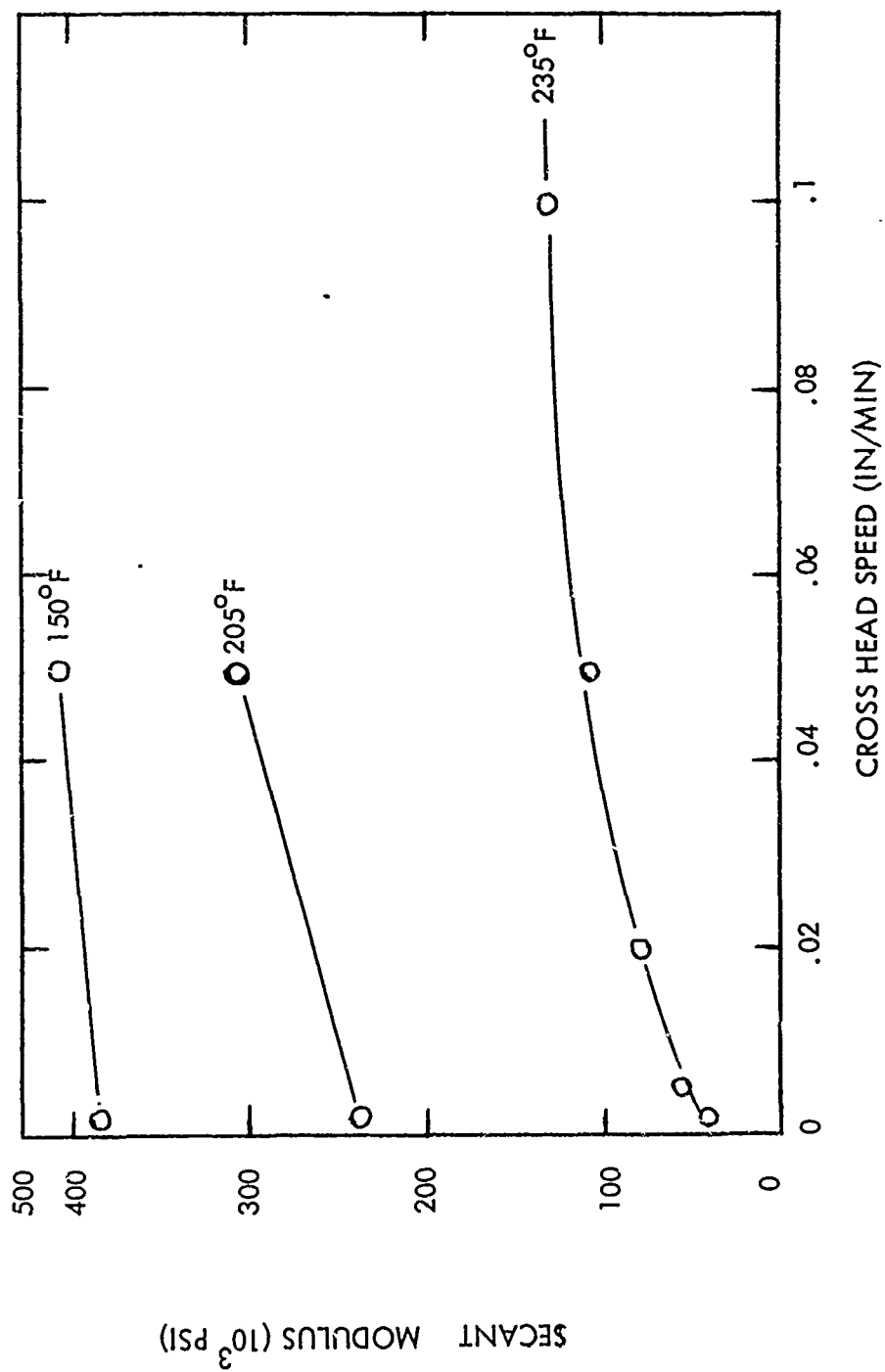
FIGURE 5

stress applied. The major part of this recovery seems to occur within a few minutes. A small bias stress of about 300 psi is always maintained to assure axially of the specimen and to keep all parts seated in the loading assembly. The effective tensile modulus values reported in Figure 5 were taken from the low stress portions of the stress-strain curves where the adhesive material was still deforming elastically. Any viscoelasticity or plastic flow did not contribute to these values of the moduli. The highest value of E^* (731,000 psi) was the initial measurement made two days after curing the joint. Subsequent values of E^* were lower as a result of the strain put in the specimen. As can be seen in Figure 5, the effective tensile modulus drops rapidly with the first increments of permanent strain. It appears that E^* is asymptotically approaching a limiting value of about 610,000 psi. There were no data available for pre-strains greater than 20×10^{-4} because the specimen was taken directly to fracture in the next test. The total strain to fracture, neglecting any unload recovery, was about 600×10^{-4} . Thus the data of Figure 5 represent only the first few percent strain of the total stress-strain curve. Fracture was of the center-of-bond type and appeared to occur at the nylon cloth/epoxy interface.

As far as is now known, these changes in E^* are permanent. There was no fixed time interval between successive increments of pre-strain; sometimes it was a few minutes, in other cases it was a few days. Within those time spans there were no time dependent effects. There has not yet been a systematic evaluation of how the adhesive properties change with time; especially with the added parameter of pre-strain. It is felt that the decrease in E^* is due to some molecular rearrangement that is responsible for and/or is caused by permanently straining the adhesive material. All of the data shown in Figure 5 were made at a single strain rate. However, strain rate should not be a factor in the elastic part of the stress strain curve. To get a load-unload cycle that shows a straight line relationship between stress and strain there can be no time dependent mechanisms operating. If there are no such mechanisms then changing the strain rate does not alter the results. A very low strain rate may allow some viscoelastic behavior, but that would not result in a linear (elastic) stress-strain relationship. Using a very low strain rate would probably have the effect of diminishing the stress range in which elastic behavior is found.

3.3 Cross Head Speed Dependence of Secant Modulus

The secant modulus of the Epon 9601 with carrier between stainless steel adherends was measured as a function of cross head speed at -10° , 75° , 150° , 205° and 235°F . The joint was made with tape having a nominal thickness of 0.012 in.; however, following cure the glue line was 13.2×10^{-3} in. thick. It has been found that there are variations in thickness of the as-received sheet adhesive so that some joints are thicker than the nominal thickness of the starting material. As shown in Figure 6, the data are given in terms of cross head speed rather than strain rate. To calculate the strain rate it is necessary to know the "stiffness" of the testing machine; or more specifically, what is the rate of travel of the adhesive/adherend interfaces for a given cross head speed. This may be determined by timing the X-Y recorder trace, for that is the displacement of the interfaces that must be known. The strain rates will be determined as a function of applied stress since the stiffness of the loading assembly may be influenced by the load it experiences. In Figure 6, results are given only for the three highest test temperatures, at cross head speeds of 0.002 to 0.1 inches per minute. At room temperature and below, the secant modulus was independent of cross head speed over the rates shown in Figure 6. It should be noted that the secant modulus was measured at stresses much smaller than the fracture stresses. For the 150°F tests, the stress range used was 250 to 765 psi; in the case of the 205°F tests, a stress range of 250 to 450 psi was employed; for the 235°F load cycles, the minimum stress was 100 psi and the maximum was 300 psi. It was necessary to limit the maximum stress at the higher temperatures to prevent excessive deformation and/or fracture of the adhesive material. If the secant modulus had been measured at higher applied stresses, the resultant values would have been smaller than shown in Figure 6. As the cross head speed was increased, the behavior at each temperature was similar, i.e. the secant modulus increased. This behavior is again a manifestation of the viscoelastic effects which occur in this system at elevated temperatures. The time required to reach a particular stress level decreases as the cross head speed increases. As a result of this time dependence, the extension at any particular stress level decreases with increasing cross head speed giving rise to a higher secant modulus.



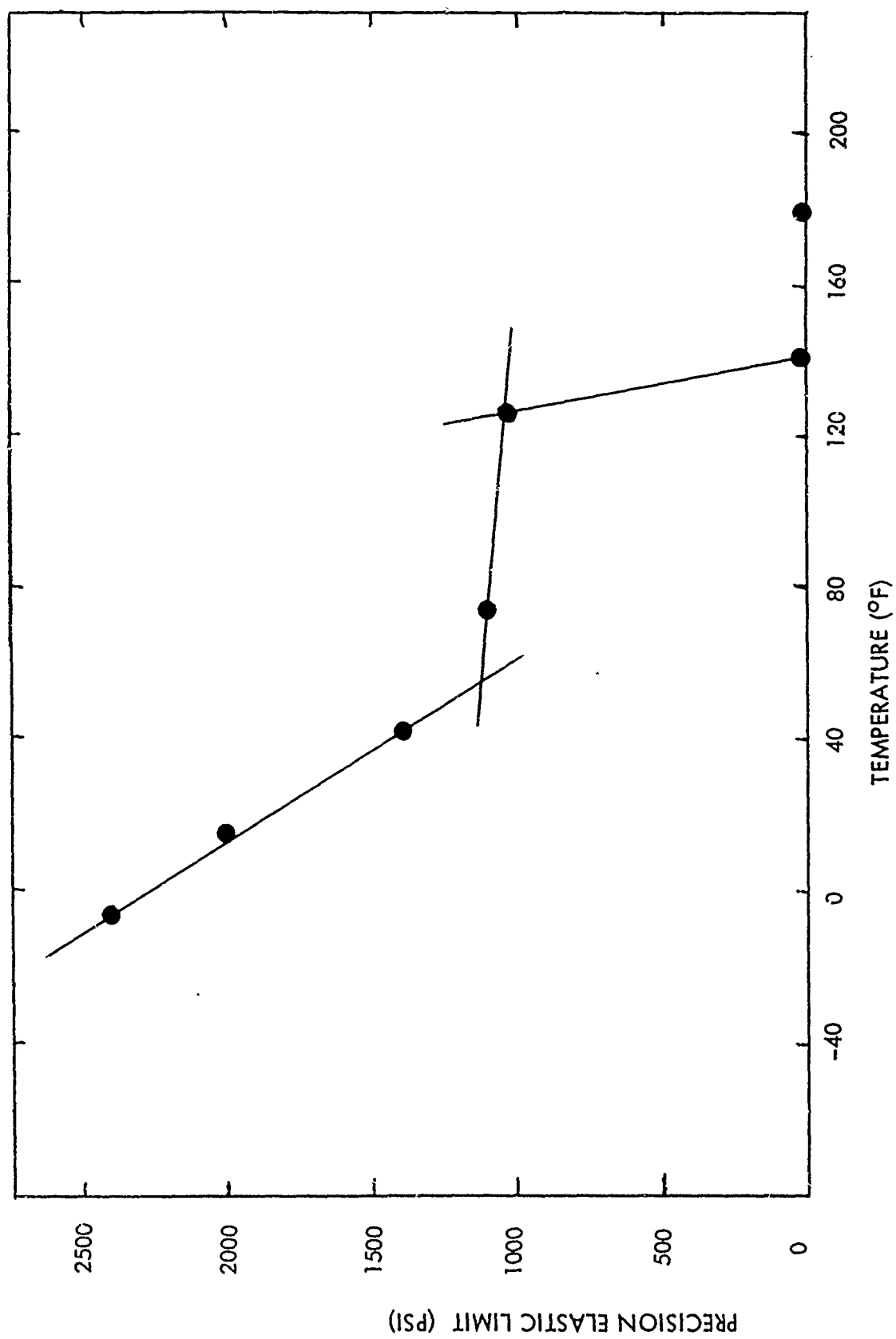
EPON 9601-TENSILE TESTS, STAINLESS STEEL ADHERENDS

FIGURE 6

3.4 Precision Elastic Limit

The term precision elastic limit (P.E.L.) is defined as the maximum stress a material may withstand and still have elastic deformation. Deviations from elasticity may be in the form of viscoelastic flow or permanent strain. The values obtained for the P.E.L. depend strongly upon the sensitivity of measurement. If insensitive techniques are used, small deviations from elastic behavior are not recognized; this results in an appreciably higher value for the elastic limit. Whenever P.E.L. values are reported, the measuring sensitivity must be included. In the work reported here, deformations as small as 5×10^{-7} in. are recorded.

The P.E.L. was studied in detail for tensile tests made with Epon 9601 (with a nylon carrier). Aluminum adherends were used, and the glue line was 8.75×10^{-3} in. thick. The precision elastic limit was measured over a temperature range of -10° to 180°F . Since the mechanical properties of this material change with pre-strain (see Section 3.2) the P.E.L. evaluation was made after the specimen had been strained about 25×10^{-4} . With this amount of pre-strain, the mechanical properties were relatively insensitive to further strain increments. Thus the load-unload cycles to establish the various microstrain properties did not introduce any significant changes in the material. The variation of P.E.L. with temperature is shown in Figure 7. At each temperature tested, load-unload cycles were made at increasingly higher applied stresses, starting just above the bias stress. At the lower stresses, the adhesive deformed elastically. The first deviations from elasticity (P.E.L.) were in the form of viscoelastic flow and were manifested as closed hysteresis loops on the X-Y recording. Referring to Figure 7, there appears to be three distinct types of behavior: 1. In the region from -10° to 55°F , the P.E.L. decreases sharply as room temperature is approached; the rate of change of P.E.L. is about 25 psi per $^{\circ}\text{F}$; 2. The second region (about 55° to 130°F) is characterized by a small temperature dependence, the change is only 1.3 psi per $^{\circ}\text{F}$; 3. For the range 140° to 200°F , the graph shows values of zero for the P.E.L., this is to indicate that no precision elastic limit could be measured. For the smallest applied stresses, considerable non-elastic behavior was observed; there were no linear stress-strain traces in this high temperature



TENSILE TESTS-EPON 9601, WITH CARRIER, ALUMINUM ADHERENDS

FIGURE 7

range. It is possible that at these temperatures there may have been deformation occurring in the Epon 9601 due to the bias stress which is always maintained. No measurements were made to illuminate this point. The time at elevated temperature was kept to a minimum to avoid the possibility of extensive flow in the adhesive; in addition, the maximum applied stress was well below that used at lower temperatures. Following the low and high temperature tests, the value of the P.E.L. at 75°F was the same as at the start of the temperature cycle. Thus no permanent changes in P.E.L. were introduced as a result of the testing procedures.

3.5 Temperature Dependence of Shear Modulus

Shear tests were carried out in the napkin ring torsion apparatus described in the Second Quarterly Progress Report. The apparatus was mounted in the environmental chamber described in Section 2. A napkin ring-type specimen was prepared using the Epon 828/Versamid 140 (30 wt percent) system in the manner previously described. As with the tensile tests, a series of load-unload cycles were first carried out at room temperature. The temperature was then raised in increments up to 210°F with load-unload tests carried out at each temperature after allowing the specimen to come to equilibrium. The temperature was lowered to room temperature in a similar step-wise fashion and the measurements were repeated. The above procedure was repeated in the cooling cycle down to -50°F and re-cycled to room temperature. The shear modulus was calculated for loads between 100 pounds and 450 pounds, using the equation previously derived in the Second Quarterly Progress Report:

$$G = 8.06 PL / \Delta s \quad (1)$$

where

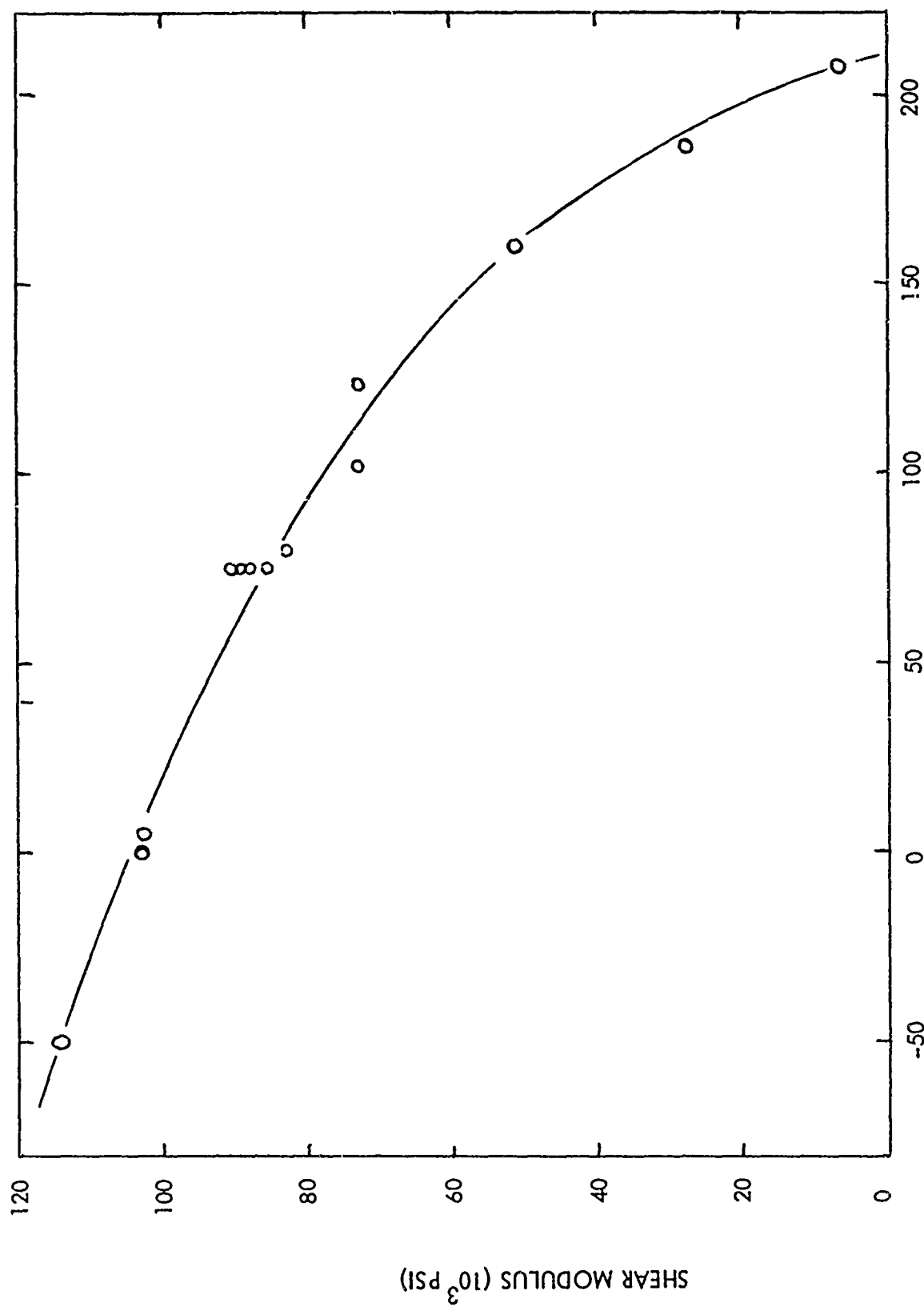
G = Shear modulus

P = Applied load

L = Specimen gage length

Δs = Displacement measured by capacitance extensometer

The results obtained for a 0.005 inch thick joint are shown in Figure 8. The shear modulus is 88,000 psi at room temperature. When the temperature is lowered to -50°F , G increases about 35% to a value of 114,000 psi. Upon returning to room temperature the original shear modulus was restored. G is more temperature sensitive above room temperature; the modulus decreases at an increasing rate as the specimen is heated. At 210°F , the shear modulus has decreased to about 15% of its room temperature value. On cooling to room temperature, the shear modulus completely recovered, indicating that the epoxy joint did not undergo any permanent change on heating to 210°F . The changes in shear modulus with changing temperature are probably due to viscoelastic effects and plastic flow which increase with increasing temperature and are minimized at the low temperatures.



EPON 828/V 140, STAINLESS STEEL ADHERENDS
FIGURE 8

4. FUTURE WORK

The fourth and final quarter of this program will be devoted to completing the thickness and temperature effects on the properties of Epon 9601 and Epon 828/Versamid 140 systems. A third material, 3M Company's EC 2214, will also be investigated.